Introduction

This report covers the period March 1, 2011 to February 28, 2012, the 46th year of the Massachusetts Water Resources Research Center (WRRC). The Center is under the direction of Dr. Paula Rees, who holds a joint appointment as Director of the WRRC and as Director of Education and Outreach of the Engineering Research Center for Collaborative Adaptive Sensing of the Atmosphere at the University of Massachusetts Amherst (UMass).

Five research projects were supported by the Massachusetts Water Resources Research Center through the USGS 104B Program. One research project, headed by Dr. Andrew Ramsburg of Tufts University, was entitled "Elucidation of the rates and extents of pharmaceuticals biotransformation during nitrification." Four graduate student projects were also funded: “A remote sensing algal production model to monitor water quality and nonpoint pollution in New England lakes” under PI Dr. Mi-Hyun Park of UMass Amherst; “Monitoring and understanding water quality at three potential Charles River swimming sites” under PI Dr. Ferdi Hellweger of Northeastern University; “Authentic research projects for undergraduates based on groundwater contamination issues related to Arsenic” under PI Julian Tyson of UMass Amherst; and “Assessing human impacts on sediment and contaminant trapping within Oxbow Lake, Northampton, Massachusetts” under PI Jonathan Woodruff of UMass Amherst.

The 104B Program also supported one Technology Transfer projects: the Eighth Annual Water Resources Conference, organized by the Water Center on the University of Massachusetts Amherst campus;

The USGS 104G Program supported a research project entitled “Characterizing and quantifying recharge at the bedrock interface” led by Dr. David Boutt of UMass Amherst.

The Massachusetts WRRC also administered three United States Army Corps of Engineers (USACE) awards to Dr. Casey Brown of UMass Amherst using supplemental funds passed through the USGS to the Water Resources Research Center. The titles of these projects are: “Evaluation of adaptive management of Lake Superior amid climate variability and change,” “Climate risk assessment and management,” and “Development of a Hydroclimate Synthesis Report for International Upper Great Lakes Study.”

Progress results for each project are summarized for the reporting year in the following sections.
Research Program Introduction

Nine research projects were conducted this fiscal year.

One research project was funded through the USGS 104G program, and three research projects received USACE funding through the WRRC. The three research projects funded by the USACE are "Evaluation of Plausible Risk to Lake Superior Regulation and Upper Great Lakes Amid Climate Variability and Change," and Development of a Hydroclimate Synthesis Report for International Upper Great Lakes Study, all led by PI Dr. Casey Brown of UMass Amherst and administered by the Water Center.

Five new projects were funded through the 104B program and were completed this year.
Characterizing and Quantifying Recharge at the Bedrock Interface

Basic Information

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Publications

Title Characterizing and Quantifying Recharge at the Bedrock Interface

Project Number 2009MA213G

Start Date 9/01/2009

End Date 8/31/2012

Funding Source 104G

Research Category Groundwater Flow and Transport

Focus Categories GW WS WQ

Descriptors Groundwater, Bedrock, Fractured-Rock Aquifers, Recharge

Primary PI Dr. David Boult

Other PIs Dr. Stephen B. Mabee

Problem and Research Objectives

The recharge of groundwater through glacial till is poorly understood (Cuthbert, 2010). Recharge occurs when the soil moisture deficit and matric potential is reduced sufficiently to allow for free draining water to enter the aquifer below the overburden layer (Rushton, 2005). The process is complicated by the presence of low permeability and often, anisotropic tills (Rushton, 2005). Researchers’ attempts to characterize recharge through till are not new and have historically relied upon regional water balance approaches that lack resolution and assume that the potential recharging water volume is equal to actual recharge volume (deVries, 2002). To complicate matters further, an observed rise in the water table may be related to recharge or may be related to a pneumatic pressure response from an increase in the overlying weight of the wetting front in the overburden (Rodhe and Bockgard, 2006). Fitzsimmons and Misstear (2006) have shown recharge coefficients, that is the amount of effective precipitation that will cause a particular amount of recharge, to vary between 2% and 80% by varying the till hydraulic properties. The thickness of the till package that overlies the receiving bedrock aquifer is equally important especially when determining the vertical hydraulic gradient for Darcy flux calculations (Stephens, 1996). White and Burbey (2006) noted that recharge rates to bedrock aquifers are controlled by the permeability of the structures found within the bedrock aquifer.

Developing an understanding of bedrock recharge dynamics is imperative to future water sustainability in communities that rely upon bedrock aquifers. Continued withdrawal from bedrock aquifers without an understanding of the timing and rate at which the aquifer is replenished could result in stifled economic development and water shortage. The purpose of this project is to understand the timing and nature of recharge to bedrock aquifers.
Methodology

Site Description
To investigate recharge mechanisms in this setting, a hillslope research area was developed at Gates Pond Reservoir, Berlin, Massachusetts within the Assabet River Watershed. The Gates Pond Reservoir (Gates Pond) is a 388,512 m² in area and provides drinking water to the town of Hudson, Massachusetts. The subwatershed that contributes to Gates Pond is 922469 m² in area and is mainly forested with some tree fruit agriculture; pasture land, and low-density suburban development (MASSGIS, 2012). The Gates Pond site enjoys both thick and thin till deposits as well as post-glacial alluvium (FIG 1).

Figure 1 – Surficial geology/topography of the Gates Pond Reservoir field site.

Gates Pond also has four bedrock wells that range in depths from 178 m – 242 m below surface level (bsl).

To understand the timing and nature of bedrock recharge, two bedrock wells (BMW1 and BMW2) were respectively instrumented with Solinst® Levelogger pressure transducers that logged the water level within the wells continuously at 5 minute intervals from May 20, 2010 until August 30, 2011. The water levels were corrected for barometric pressure to obtain the potentiometric surface within the bedrock aquifer. Hourly precipitation data was obtained from the National Oceanic Atmospheric...
Administration’s (NOAA) National Climatic Data Center (NCDC). Precipitation data was collected from the Fitchburg Municipal Airport (FMA) located approximately 13 miles to the northwest of Gates Pond Reservoir. Daily Potential Evapo-transpiration (PET) rates were determined using temperature data from the FMA weather station and calculated using methods developed by Thormhaite (1939). Soil moisture was also monitored continuously at 5 minute intervals from October 27, 2010 until September 9, 2011 at depths of .5 meters and 1.5 meters bsl at the thin and thick till sites using a Decagon Devices® 5TM soil moisture probes. It was assumed that the 1.5 meter soil moisture data would approximate the soil moisture conditions at the surficial/bedrock interface. Soil samples were taken at a depth of 1.25 meters bsl at both the thin and thick till sites as well as the thin till deposit that overlies the bedrock monitoring wells and were analyzed for unsaturated hydraulic properties (i.e. Van Genuchten parameters) using Decagon Devices® HyProp instrument. The unsaturated properties taken from the HyProp instrument will be used to develop a time series of unsaturated conditions in the subsurface. Finally, a transient 1-dimensional infiltration model using the HYDRUS 1-D code (Simunek et al., 2008) will be developed using the unsaturated properties of the thin and thick tills to verify the timing and magnitude of fluxes beneath the approximated surficial/bedrock interface.

**Preliminary Findings and Significance**

Work on this project began on September 1, 2009 with site selection and characterization and continues today with model development. Figure 2 includes a site locus as site map showing the location of monitoring equipment as well as geophysical survey lines. Time series data collected from wells BMW1 and BMW2 have captured bedrock recharge timing and magnitude at the Gates Pond Site (Fig. 3).

![Site map of the Gates Pond Reservoir.](image)

**Figure 2.** Site map of the Gates Pond Reservoir. In the lower left corner is a site locus showing the location of Gates Pond in relation ship to the Nashoba Formation in Massachusetts.
Figure 3. Time series of normalized head from BMW1 and BMW2. Potential evapotranspiration rate as calculated using the Thornthwaite approximation and precipitation rate are also plotted.

Summer precipitation events can have an appreciable effect on the trend of the bedrock head. Bedrock recharge occurs not only during times with reduced potential evapotranspiration but when there is a soil moisture gradient within the soil profile (Figure 4). It appears that there is a greater correlation between the soil moisture gradient and the magnitude of the recharge event than the magnitude of the precipitation and the magnitude of the recharge event (Figure 5a and 5b).

Figure 4. Plot of bedrock head within BMW1 and BMW2 along with the soil moisture gradient within thin till. Thin till is the deposit type that overlies BMW1 and BMW2. Soil moisture probes S1SMB.5 and S1SMB1.5 are collocated within the thin till at .5 meters bsl and 1.5 meters bsl respectively.
Figure 5a  Correlations between soil moisture gradient and magnitude of bedrock recharge event.

Figure 5b  Lack of correlation between magnitude of precipitation event and bedrock recharge event.

Soil moisture retention curves of the thin and thick tills were also determined using the Decagon Devices HyProp device and the unsaturated hydraulic properties were determined using Brooks and Corey (year) (Figure 6)
Figure 6a. Soil moisture retention curve for thin till deposits.

Figure 6b. Unsaturated hydraulic conductivity of the thin till.
Once the soil moisture retention and unsaturated hydraulic conductivity curves were developed, a time series of unsaturated hydraulic properties was developed (Figure 7).

**Figure 7.** Time series of matric potentials and hydraulic conductivities.

**Bedrock Hydroclimatic response:**

In order to constrain the regional subsurface response of bedrock ground water flow systems, we need to first understand relationships between hydroclimatic variables (such as temperature and precipitation) and surface and subsurface hydrology (i.e. streamflow and ground water) in overlying sediments. Research by the PI using distributed networks of ground water wells has yielded valuable information regarding hydraulic ground water response to climate. Following Weider and Boult (2010) we calculate air temperature, precipitation, streamflow and ground water anomalies ($A_j$), defined as $A_j = m_j - \bar{m}$ where $m_j$ is the monthly value, $\bar{m}$ is the average for an individual month over a time series, and normalized anomalies ($NA_j$), defined as $NA_j = \frac{m_j - \bar{m}}{\sigma_m}$, where $\sigma_m$ is the standard deviation for the individual month over the whole time series. To look at
longer term and seasonal averages, we use 12-month moving averages fit to monthly normalized and anomaly values. Weider and Boult (2010) present ground water data from 100 well sites that span across the US New England region with sites selected to be within differing geologic, watershed, and climatic environments. Figure 2 displays all selected sites, which include 43 air temperature sites, 75 precipitation stations, 67 stream gages and ground water sites. Strong inter-relationships between the anomalies in climatic variables (temperature, and precipitation) and hydrologic variables (streamflow and ground water) exist for sites across the study region (Figure 3). Weider and Boult (2010) showed that the ground water sites display more variation about the mean (i.e. standard deviation) and have almost twice as much variability as air temperature, precipitation, and streamflow. We plan to utilize this set of wells to explore subsurface temperature variability due to the hydrologic and hydrogeologic factors discussed below.

The region-wide anomalies depict strong relationships between precipitation, streamflow, and ground water and illustrate a strongly advective ground water environment. As discussed in Weider and Boult (2010) a progression from small to large negative anomalies exists in increasing order from precipitation to streamflow to ground water anomalies, which is more obvious during periods with major droughts (i.e. 1960’s and 1980’s). During periods with positive anomalies, these differences are not observed and streamflow and ground water anomalies strongly track one another.

Figure 9: Normalized anomalies for the hydroclimatic data presented in Figure 2. These lines represent the average of all sites and record periods of dry (D) and wet (W) times.

A close examination of Figure 3 indicates that during times of negative anomalies, a consistent progression from low to high negative anomaly magnitude is apparent when comparing precipitation to streamflow and then to ground water anomalies (e.g. during the mid 1960’s and
early 1980's). During periods of positive anomalies these trends are also apparent, but the difference in magnitude between streamflow and ground water is not significant for reasons discussed above. The trend of increasing negative and positive anomaly magnitudes is puzzling, as climate drivers (such as precipitation) often show larger magnitude anomalies than ground water due to precipitation's highly non-autocorrelated nature (El-tahir and Yeh, 1999). Ground water systems are often called upon to moderate climate forcing, acting as a low-pass filter. Yet, these data suggest that ground water response is amplified relative to both air temperature and precipitation responses.

The regional water table hydraulic anomalies are controlled by the hydraulic properties of the material that the well is screened within and whether the well is screened in a recharge or discharge area of the aquifer. The hydraulic properties of the aquifer material influence the magnitude and rate of recovery of the water table anomaly. These include infiltration properties of the soil, specific yield, aquifer hydraulic conductivity, and regional hydraulic gradient. We anticipate that these factors will also influence the temperature characteristics of the subsurface.

The time series presented in the top of Figure 5 are generated by taking the anomaly for an individual month and averaging them for well sorted sand and gravel and poorly sorted silt, sand, and gravel for the time period of 1956 to 2010. The two time series have similar overall patterns recording transitions between wet (positive) and dry (negative) periods in the record. For both composite series, the minimum anomaly is always of a greater magnitude than the maximum anomaly. A distinct and measurable difference exists between wells screened in sand and gravel dominated aquifers and those screened in till (poorly sorted silt, sand, and gravel).

Water levels in discharge regions are influenced by nearby surface water and up-gradient groundwater conditions. In contrast recharge regions display large fluctuations in water level due to primarily vertical flow paths. In humid temperate climates, the water table strongly mimics topography: with shallow water tables in areas of low relative topography and deeper water tables in areas of higher relief (Gleeson et al., 2011). Averaged time series for 3 groupings are presented in

![Figure 10](image-url)
Figure 5 (bottom). In general the time series are highly correlated and have similar trends during both dry and wet periods. A few important distinctions can be discerned: 1) deeper water tables have larger minima and maxima, 2) A lag of 2-5 months is apparent as the deeper water tables lag shallow water tables consistently, 3) this lag increases with the magnitude of the minima (drought severity), and 4) the slopes of the transitions for the three groupings are very similar. Since deeper water tables are assumed to be in recharge areas, these trends suggest that recharge areas and discharge areas have significantly different responses to climate variability. The lags and the timing of high and low anomalies imply a time-dependent water table response to climate that will also control how heat is advected into the subsurface.

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<td>Multi-seasonal and distributed networks of subsurface temperature measurements yield valuable information on the hydrologic and hydrogeologic structure of shallow ground water basins but usually do not yield insight into local-scale recharge processes, their effects on the heat budget, or the degree of near-surface coupling between air and ground temperatures. Our research group has been intensively monitoring a local watershed adjacent to a water supply reservoir in Berlin, Massachusetts, USA to understand deep recharge processes and subsurface temperature responses. Figure 7A represents a time series of soil temperatures and ground water temperatures for the summer of 2011, when precipitation was almost 175% of normal. Ground water temperatures (red –shallow, black–deep) from two wells record the seasonal warming of the near-surface ground water. However, during periods of recharge (when shallow heads are greater than deep and soil moisture flux is high – gray boxes) these ground water temperatures are perturbed. During these conditions, shallow ground water temperatures are increased due to the inclusion of warmer recharge water, and deeper ground water temperatures are decreased, possibly due to advection of cooler water from depth reflecting a complex interplay of near-surface coupling and advection of water.</td>
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Figure 11: Soil and ground water temperatures (A) respond to seasonal heating and recharge events due to advection of water (B).

**Future Work**

We are currently installing two additional bedrock monitoring wells at a new site in Whately, Mass. While installing the well, the bedrock/till interface will be cored and characterized. The new bedrock well will be instrumented with fiber optic DTS probes as well as instrumented to measure hydraulic head at multiple depths. The well will also be geophysically logged for resistivity, with a heat pulse flow meter, imaged and interpreted via optical televiwer and caliper. Time series data will continue to be collected and analyzed from all wells, soil probes and the pond. Stable isotope analysis will also be performed from regular sampling at the site. Stable isotopes will give the Investigators insight as to the
origin of the water onsite and will allow the investigators to determine whether responses in bedrock wells are the result of advection across the bedrock/till interface or an expression of the pressure wave associated with hydraulic diffusion and surface loading of meteoric water mass.

**Publications and Conference Presentations**


Boutt, D.F. and K. Weider, Regional-Scale Water Table Response to Decadal Climate Variability, In preparation for submission to J. Hydrology.

Boutt, D.F and L.B. Bevan, A conceptual model for the hydrologic connection of glacial derived surficial materials to fractured crystalline bedrock, In preparation for submission to Ground Water.


**Student Support**

Data collected from the bedrock core will be the centerpiece of Amy Hudson’s PhD degree looking at fluid flow through fractures.

Liam B. Bevan is fully supported by this project. He is pursuing an M.S. degree in geology in the Department of Geosciences at the University of Massachusetts, Amherst.

Evan Earnest-Heckler is partially supported by this project. He has been assisting with field work and developing a detailed characterization of the fractured bedrock of the site. He is pursuing a PhD in geology in the Department of Geosciences at the University of Massachusetts, Amherst.

Shakib Ahmed used data collected from this project for his Senior thesis. He completed his B.S. in geology in the Department of Geosciences at the University of Massachusetts, Amherst.

**References**


USGS Award No. G10AP00091 Evaluation of Adaptive Management of Lake Superior amid Climate Variability and Change

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Publications

Title: Evaluation of Adaptive Management of Lake Superior amid Climate Variability and Change

Project Number: USGS Award No. G10AP00091

Problem and Research Objectives:
Provide a systematic, quantitative assessment of adaptive management strategies for the International Upper Great Lake Study using historical data, stochastic analysis and climate change projections.

Methodology:
1. Using historical data and stochastic analysis, characterize the response of Lake Superior and the Upper Great Lake System (Superior-Michigan-Huron) to generalized climate variability and change
   a. Based on findings from ongoing and completed studies, identify the climate forcings of interest on the Lake System (e.g., monthly precipitation, annual mean temperature, etc.)
   b. Produce “response surfaces” of Lake System response to climate through simulation using parametrically varied climate forcings.
   c. Identify dominant climate variables based on the simulated impact of each variable on Lake System performance.
   d. Identify critical timescales of variability (including low frequency variability and trends) that significantly affect system performance. Identify threshold values of climate variable that significantly alter system performance.
2. Use climate information generated from General Circulation Model output, historical climate analyses and other model simulations to estimate risks associated with the dominant climate influences identified in Part 1.
   a. Generate estimated probability density functions for variables of interest and timescales of interest using GCM output
   b. Assign probabilities to ranges of climate variables of interest
   c. Estimate risks associated with specific climate influences
3. Assess Adaptive Management Approaches in response to anticipated climate variability and changes.
   a. Using current and proposed regulation plans including fence post plans, evaluate range of performance dominance for each strategy over ranges of climate variables of interest.
   b. Identify climate thresholds where regulation plan optimality changes based on climate conditions using Bayesian decision model.
   c. Assess performance of adaptive management strategies (including regulation plan switching in accordance with change points identified in part b) and static management strategies (a single optimal regulation plan) using historical data, stochastic analysis and climate change risk projections.
   d. Estimate probable dominant adaptive and static management strategies for historical (stationary) and climate change (via GCM-based pdfs) conditions.

Principal Findings and Significance:
The analysis defined a new way to conduct climate risk assessments for large water resource systems.
Student Support
The funding provided partial support for 1 MS and 1 PhD student.

Notable Achievements and Awards

Publications and Conference Presentations:
Provide citations for publications resulting from all projects supported using your grant and required matching funds, including base grants. Please provide the citations in the format requested.

a. **Articles in Refereed Scientific Journals**

b. **Book Chapter**

c. **Dissertations**

d. **Water Resources Research Institute Reports**

e. **Conference Proceedings**

f. **Other Publications**
A Remote Sensing Algal Production Model to Monitor Water Quality and Nonpoint Pollution in New England Lakes

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Publications

1. Adam Trescott and Mi-Hyun Park, Satellite Image Application to the Spatial and Temporal Distribution of Algal Blooms in Lake Champlain, Water Science and Technology, under review
2. Adam Trescott, Remote Sensing Models of Algal Blooms and Cyanobacteria in Lake Champlain, Master of Science in Civil Engineering, February 2012
4. Adam Trescott and Mi-Hyun Park, Remote Sensing Models Using Landsat Satellite Data to Monitor Algal Blooms In Lake Champlain, 8th Annual Water Resources Research Conference, University of Massachusetts Amherst, April 7, 2011
Annual Report (from March 1, 2011 to February 28, 2012)

A Remote Sensing Algal Production Model to Monitor Water Quality and Nonpoint Pollution in New England Lakes

Problem and Research Objectives:
Many lakes in New England suffer algal blooms because of agricultural and urban runoff and wastewater discharges. Algal blooms deplete oxygen levels and degrade the quality of receiving waters. Algae also cause discoloration and foul taste in drinking water supplies and toxins that are capable of poisoning animals and/or humans. Therefore there is a need for regional algal monitoring programs to manage water resources and protect human health.

Traditional algal bloom monitoring usually requires shipboard field sampling programs accompanied by laboratory analyses to determine in situ concentrations of aquatic chlorophyll \(a\), a photosynthetic pigment used as a proxy to measure algal biomass (Coskun et al., 2008; Carlson, 1977). The time and resources required to effectively monitor a lake’s algal blooms in situ limit the spatial and temporal resolution of these datasets. Large algal blooms often shift and change composition dramatically in a short period of time, influenced by rainfall and wind, among other factors, and measured algal concentrations may not be representative of levels throughout the lake (Shafique et al., 2001).

Satellite measurement is especially useful in lakes and inland waters because of the inherent spatial heterogeneity of phytoplankton (Ekstrand, 1992). The unique spectral absorbance/reflectance characteristics of chlorophyll-\(a\) provide a means to measure blooms over large areas at a temporal and spatial resolution unattainable by field methods (Richardson, 1996; Park and Ruddick, 2007). This study will develop a bio-optical model specific to Lake Champlain using available in situ and satellite data. The model will provide for timely and cost-effective monitoring of algal bloom distribution in the lake.

Alternatively, we used satellite remote sensing for regular, synoptic coverage of algal blooms because satellites can scan entire regions of the earth with frequent revisit times. The objectives of this study are to establish an effective satellite algal production model that can be used to remotely monitor the spatial and temporal distributions of algal blooms in Lake Champlain and to evaluate the predictive ability of the satellite model.

Methodology:
The study area is Lake Champlain, bordered by New York, Vermont and Quebec, Canada, a good case study for a New England lake because blooms of algae and cyanobacteria (also called blue-green algae, one of the harmful algae) have become an increasing problem in the lake over the past two decades. The models developed in this study are based on in situ water quality data for Lake Champlain, obtained from the Vermont Department of Environmental Conservation and the Lake Champlain Basin Program between 2006 and 2009.

We conducted satellite image remote sensing using Landsat Enhanced Thematic Mapper Plus (ETM+) images obtained from the U.S. Geological Survey Earth Resources Observation and Science Center. A satellite overpass time window of \(\pm 1\) day was used to establish coincident pairs and processed with ENVI (Ver. 4.7, ITT®) and ArcGIS (Ver. 9.3, ESRI®). All satellite images of coincident pairs from in situ sampling data were converted to exoatmospheric reflectance for standardized comparison of data among multiple images.

The remote sensing chlorophyll \(a\) algorithms were developed based on step-wise multilinear regression with single-band input and non-reciprocal reflectance band-ratios. The regression models were calibrated and cross-validated using coincident pairs from the late summer bloom period (July 20\(^{th}\) to September 10\(^{th}\)), obtained between 2006 and 2009. The best single band and band-ratio models were then applied to entire satellite scenes to estimate chlorophyll \(a\) and algal blooms for the entire lake.
Principal Findings and Significance:
The regression models provided the most significant band information of satellite imagery for detecting chlorophyll $a$ pigments that can be used for estimating algal blooms. The final chlorophyll-$a$ models based on the single band model and band ratio model are presented by the following equations:

$$\text{chlorophyll } a \ (\mu g \ L^{-1}) = 14.37 - 685.19(R_{B1}) + 905.94(R_{B2})$$  \hspace{1cm} (1)

$$\text{chlorophyll } a \ (\mu g \ L^{-1}) = -46.51 + 105.30(R_{B2}/R_{B1}) - 40.39(R_{B3}/R_{B1})$$  \hspace{1cm} (2)

where $R_{B1}$, $R_{B2}$ and $R_{B3}$ are the normalized exoatmospheric reflectance values for Landsat ETM+ bands 1, 2 and 3, respectively. $R_i/R_j$ stands for the reflectance ratio of the $i^{th}$ band over the $j^{th}$ band.

The single band model regression model (Eq.1) showed green band (B2) and blue band (B1) to be the most significant chlorophyll $a$ predictors. This is a key difference from other studies. Previous studies had found Landsat’s red-sensitive band (B3) useful in single band chlorophyll $a$ models because it is least sensitive to atmospheric effects, yet it has the lowest penetration distance in the water column (Richardson, 1996; Sass et al., 2007). The regression model with Band 2 and Band 3 gave similar coefficients of determination ($R^2$) but higher root mean square errors. The difference is likely due to the collection method of chlorophyll $a$ water samples in Lake Champlain. All chlorophyll $a$ samples were collected as representative composites of the photic zone, defined as twice the Secchi depth at the time of sampling. The higher water column penetrations achieved by Landsat ETM+ bands 1 and 2 may give better predictions of phytoplankton present in the entire photic zone rather than surficial concentrations collected via grab sampling. It should be noted, however, that ETM+ bands 1 and 2 are more susceptible to atmospheric interference, therefore limiting this single band model to clear sky coincident pairs.

The band ratio model (Eq. 2) slightly outperformed in terms of $R^2$ the single band model by using the ratio of the chlorophyll $a$ green reflectance peak to the blue reflectance minimum, as well as the ratio of the red reflectance trough to the blue reflectance minimum. These two ratios maximize the effects of three distinctive optical features of chlorophyll $a$. The improved performance of the band ratio model over the single band model agrees with the findings of past studies (Vincent et al., 2004) that found more robust results using band ratios. The algal models based on regression analysis also provide similar results.

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The resulting algal model was applied to satellite imagery to estimate the chlorophyll $a$ and algal blooms. Figure 2 shows a time series of resulting Landsat ETM+ images for chlorophyll $a$ and algal blooms in Missisquoi, one of the most eutrophic areas of lake. The results provide the distribution and propagation of chlorophyll $a$ and algal blooms. The results of bloom patterns from July 24, August 9 and August 24 show significant concentrations forming in the northeastern side of the Bay, in close proximity to a major tributary (Pike River) while the result on September 10 shows significant concentrations forming in the southern side of the Bay, in close proximity to a major tributary (Missisquoi River). The July and September images show the most intense blooms compared to August. Our approach demonstrates the utility of the satellite based algal models for the purposes of bloom detection and monitoring. The spatial distribution of algal blooms shows similar patterns compared to the distribution of chlorophyll $a$. 
The Landsat ETM+ model results were also used to assess how precipitation and river discharge impact bloom formation in Missisquoi Bay. Figure 3 shows daily precipitation data (NOAA NCDC) at Philipsburg station in Canada, located in the vicinity of Missisquoi Bay from July 10 to August 10, 2006 plotted. The data show that the impact of precipitation events on chlorophyll $a$ blooms, which are inferred by the model results near the outlets of two major tributaries that discharge to Missisquoi Bay. On July 24, high chlorophyll $a$ blooms were detected near the outlet of the Missisquoi and Pike Rivers whereas on August 9, the areas around the outlets of the Missisquoi and Pike Rivers are very low in cyanobacteria, with higher concentrations forming along the central and eastern portion of the bay. Between the July 24 and August 9 Landsat 7 ETM+ flyovers, a significant precipitation event (0.46 inch) occurred on July 22, just two days before the flyover on July 24. The introduction of nutrients in the stormwater runoff on July 22 likely caused the blooms near the outlets. Between July 31 and August 1, severe precipitation (0.45 inch and 0.90 inch, respectively) occurred about a week before the Landsat flyover on August 9. After the large storm, the distribution of the blooms could shift and subsequent dry days and a small precipitation event (0.07 inch) on the day before the August 9th flyover likely lead to low levels of blooms at the mouths of the two rivers. The bloom initiation and propagation in Lake Champlain could shift within a week. More research should be conducted to confirm this theory, but it demonstrates the power of synoptic coverage of cyanobacteria in determining the drivers of algal blooms.
This study demonstrates how remote sensing models can be developed for lake monitoring programs at relatively low cost. Moreover, our results serve as basis for retrospective study when in situ data are not available and provide important information for Lake Champlain resource management. The result can be used for further study to identify the major drivers of algal blooms; and to use it in the early detection of algal blooms.

References

Student Support
Adam Trescott, Master student, Department of Civil & Environmental Engineering, UMass Amherst
Elizabeth Isenstein, Master candidate, Department of Civil & Environmental Engineering, UMass Amherst

Notable Achievements and Awards
This fund was used to conduct current research and support students. The results in this study have been used to prepare new proposals and will be used to prepare NSF Career Award for preliminary research. The results were also used to present at the workshop for Lake Champlain stakeholders and researchers: “Bay and Basin Missisquoi Bay”.
Monitoring and Understanding Water Quality at Three Potential Charles River Swimming Sites

Basic Information

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Publications

3. Xiaodan Ruan, Sarah Sanchez, Kellie Burtch, Diana Cost, Rebecca Powers, Julia Leung, Robert Cost, Ferdi Hellweger. 2012. Swimming in Urban Rivers in the US is no longer an Imagination— a two-year case study of Charles river. RISE 2012: Research and Scholarship Expo, Northeastern University, Boston, MA (Poster).
Monitoring and Understanding Water Quality at Three Potential Charles River Swimming Sites

Xiaodan Ruan (PhD student) and Ferdi L. Hellweger (PI)

Introduction

The Charles River has a long and often publicized history of pollution, and has been closed for primary contact (swimming) for about 80 years. In 1995 the US EPA established the Clean Charles River Initiative with the explicit goal of making the river swimmable by 2005. The EPA’s prioritization of the Clean Charles River Initiative led to a massive public investment of over $500 million dollars by the MWRA, BWSC, and other utilities, as well as adjacent municipalities, over the past decade and a half. This clean-up effort has resulted in improved water quality - to the extent that swimming is now a real possibility. In 2009 the Massachusetts legislature established the Charles River Water Quality Commission to study the feasibility of returning public access swimming to the Charles. On a broader scale, opening up a swimming location on the Charles River would make it one of the first urban rivers in the US to be fully reclaimed from pollution to support swimming.

An important task is to determine the water quality at candidate swimming locations. A number of ongoing monitoring efforts (e.g. Charles River Watershed Association, CRWA) provide data, but only at a relatively coarse spatial and temporal resolution. To determine the water quality at specific swimming locations at a high temporal resolution, we performed water quality monitoring in Summer 2010. That project provided some insight into the water quality, but also identified additional research needs.

Results from 2010 Monitoring

The Summer 2010 project included monitoring of *E. coli*, turbidity and temperature at 5 potential swimming locations, including Riverside Boat Club (proximity Magazine Beach), MIT Sailing Pavilion, Esplanade Dock, Lee Pool and New Basin. This included daily monitoring by grab sampling as well as hourly monitoring using two ISCO autosamplers. Some results are presented in Table 1 and Figure 1.

Table 1. Summary of Violations of Swimming Criteria (235 CFU/100mL)

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<tr>
<th>Site</th>
<th>Daily</th>
<th>Hourly</th>
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<tr>
<td>Riverside</td>
<td>11%</td>
<td>31%</td>
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<tr>
<td>MIT</td>
<td>8%</td>
<td>6%</td>
</tr>
<tr>
<td>New Basin</td>
<td>3%</td>
<td>0</td>
</tr>
<tr>
<td>Lee Pool</td>
<td>24%</td>
<td>-</td>
</tr>
<tr>
<td>Esplanade</td>
<td>8%</td>
<td>1%</td>
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Fig. 1. Daily & Hourly *E. coli* at Riverside

Some conclusions from the 2010 sampling include:

1. The water quality at the 5 locations differs significantly (Table 1), which helped narrow down the list of potential swimming locations (e.g. Lee Pool is not a good location).
2. *E. coli* increases after large storms (Figure 1), consistent with past monitoring data.
3. *E. coli* can vary significantly within a 24-h period (Figure 1), so daily data may not be representative.
4. 18-h counts are highly correlated to 24-h counts ($R^2 0.96-0.99$), so mid-day *E. coli* densities on one day can be available in the morning of the next day.
5. ISCO autosampler results, which exceed the 6-h holding time, are in reasonable agreement with daily grab samples, so this seems to be a feasible monitoring method.

**Additional research needs: Monitoring and data analysis**

- The 2010 results provide some insight into the water quality at the candidate swimming locations, but more research is needed. Specifically, our sampling period included only a small number of large storms (Figure 1) and no medium storms (0.5-1.0 in). Additional data are needed to characterize the water quality over a wider range of precipitation events.
- Even with an additional summer of monitoring, the database will be limited. One potential solution is to relate the water quality at the candidate swimming locations to those of other long-term monitoring efforts. For example: It may be that the *E. coli* density at MIT is typically twice that of CRWA's Mass Ave location. This would allow for the relation of our data to the long-term record and the statistical models developed by CRWA.
- Once the best swimming location has been identified and implemented, it has to be managed using a beach closing model. Those models are typically regression equations of *E. coli* density to various meteorological parameters (mostly rain). Our data show that the water quality can change significantly within a day and previous research (Hellweger and Masopust, 2008) show that this may be due to dam operation and/or wind. The data need to be analyzed considering those variables.
- In addition to *E. coli*, cyanobacteria blooms have been identified as a threat to swimming in the Charles. As with *E. coli*, several monitoring efforts are characterizing cyanobacteria cell densities and toxin concentrations, but no information is available at candidate swimming sites.

**Nature, Scope, and Objectives of the Research**

In Summer 2011, we performed daily sampling of *E. coli*, turbidity, temperature, cyanobacteria cell counts, temperature, turbidity and nutrients at three potential swimming locations from June 1 through August 15. In addition, we deployed an ISCO autosampler for hourly sampling.

The 2010 and 2011 data are being analyzed for relation to long-term monitoring data collected by CRWA and MWRA, and considering dam operation and wind variables.

**Results**

The 2011 sampling significantly expanded (doubled) the database of water quality at candidate swimming locations, and helped tie it into other monitoring efforts and contributes to understanding trends. These results are of critical importance to determine the feasibility of swimming, locating the most promising site and developing a management program.

The resulting database consists of about 2,000 *E. coli* data points. The data allowed us to quantify differences in water quality between the potential swimming locations. We also observed that best correlation between *E. coli* and precipitation was found by lagging the precipitation by one or two days. The hourly data can show significant variability within the day, with typically higher concentrations at night. Our cyanobacteria data reveal strong dynamics, including blooms and population crashes, the
causes of which are not immediately clear. Unlike for *E. coli*, we don’t have a good understanding of what drives the dynamics of cyanobacteria.

We are presently analyzing the data and are preparing a manuscript for publication in a peer-reviewed journal.

We co-organized workshop entitled "Swimming-related water quality in the Charles River" at EPA/NE, Chelmsford, MA.

**Student Support**

One graduate student pursuing PhD in Civil Engineering at Northeastern University.
Two high school students.
Two high school teachers.

**Notable Achievements and Awards**

PI Hellweger was awarded the 2012 Environmental Merit Award by the EPA, for his research on the water quality of the Charles River.

PI Hellweger submitted a proposal to NSF/CMMI entitled "Collaborative Research: Identification and Model (in)Validation of a Class of Switched Nonlinear Systems with Applications to Urban Water Quality". The proposal is pending.

PI Hellweger and graduate student Ruan were awarded the 2011 Volunteer Recognition Award by the Charles River Conservancy, for their research on the water quality of the Charles River.

**Publications and Conference Presentations:**

a. **Articles in Refereed Scientific Journals**


b. **Book Chapter**

c. **Dissertations**

d. **Water Resources Research Institute Reports**

e. **Conference Proceedings**

f. **Other Publications**


Elucidation of the Rates and Extents of Pharmaceutical Biotransformation during Nitrification

Basic Information

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Publications

Progress Report  
March 1, 2011 to February 29, 2012

Problem and Research Objectives:

Reduction of nutrient discharges and, more generally, management of the nitrogen cycle are challenges currently faced by the Nation’s community of water professionals (NAE, 2008). In the Northeast United States, impacts of excess nutrients on water quality in the Long Island Sound and Narraganset Bay have resulted in the promulgation of strict limits on nutrient discharges within the States of Connecticut and Rhode Island, respectively. Within the Commonwealth of Massachusetts the Department of Environmental Protection (MADEP) has suggested that the development of total maximum daily loads for nutrients and the management of nutrient discharges are among its priorities for the next two decades (MADEP, 2008b). In fact, MADEP is evaluating options for stringent nitrogen standards (TN < 5-8 mg/L) for wastewater treatment plants within the Connecticut River watershed, the Blackstone River watershed, and the Ten Mile River watershed (MADEP, 2008a).

Overlain in both space and time with the challenges related to nutrient control is the emerging challenge of understanding and mitigating the influence of microconstituents on human and environmental health (Schwarzenbach et al., 2006). The occurrence of microconstituents in the environment is now receiving significant attention across the engineering, science, and lay communities (e.g., Daughton and Ternes, 2000; Kolpin et al., 2002; Associated-Press, 2008). In its landmark national reconnaissance, the USGS established the presence of microconstituents in surface water bodies across the country including several water bodies located within the Commonwealth of Massachusetts (Kolpin et al., 2002). A more recent USGS survey on Cape Cod detected 43 microconstituents among 14 sampling sites that included wastewater influents and drinking water supplies (Zimmerman, 2005).

Pharmaceutically active compounds are particularly concerning as microconstituents because the explosion of development and use of these chemicals over the last 30 years, and a growing body of evidence that suggests: (i) pharmaceuticals are neither fully removed nor fully transformed in conventional wastewater treatment plants (Heberer, 2002; Ternes et al., 2004; Stephenson and Oppenheimer, 2007); and (ii) chronic exposure, even at concentrations on the order of ng/L, may have adverse effects on ecosystems, such as impaired embryo development and modification of feeding behavior (Cleuvers, 2003; Kostich and Lazorchak, 2008; Quinn et al., 2009). Recent research suggests that pharmaceuticals may be better removed where wastewater treatment is designed to meet stringent regulations on nitrogen discharge (Clara et al., 2005; Joss et al., 2005; Kimura et al., 2005). Unfortunately, however, the vast majority of studies examining the fate of pharmaceuticals through the wastewater treatment process focus on the disappearance of the parent compound. Only a few studies have attempted to elucidate the biochemical processes responsible for pharmaceutical degradation and the biodegradation products formed by these processes (Zwiener et al., 2002). Thus, there is a need for mechanistic research to elucidate the processes that degrade or remove pharmaceuticals during nutrient removal.

The overall objective of the project is to fill key data gaps related to the whether or not nitrifying bacteria are partially responsible for observations of pharmaceutical degradation in treatments designed for enhanced removal of nutrients. This overall objective will be met by focusing on three specific objectives: (i) elucidation of the rates of pharmaceutical attenuation by nitrifying organisms, (ii) identification of the metabolites produced during the nitrification process, and (iii) development of modeling tools for prediction of pharmaceutical degradation within the context of enhanced nutrient removal.

Methodology:

A series of batch experiments are being conducted to evaluate the sorption and biodegradation of five selected pharmaceuticals (atenolol, diazepam, metoprolol, naproxen and sotalol) in nitrification activated sludge systems. Note that topiramate was replaced by sotalol (a beta-blocker) as the latter is more relevant to this project. Evaluation of sotalol, along with atenolol, and metoprolol will enable us to assess attenuation within a
family of beta blockers that differ by one-to-two functional groups, which our initial experiments suggest has an important influence on the degradation (see results below).

Pharmaceutical sorption is being evaluated using batch experiments setup in 30 ml foil covered glass vials with teflon caps. Each vial contains mixed liquor from our nitrification SBR and the target pharmaceutical at concentrations in the range of 500 ng/L to 50 ug/L. Sorption of the pharmaceutical at each concentration is assessed in triplicate. Homogenous samples are collected every six to eight hours. Samples are centrifuged and the pharmaceutical concentration in the aqueous phase is measured. The sorbed pharmaceutical concentration (ug /g-suspended solids) is calculated. Equilibrium is considered to have been achieved when the measured aqueous pharmaceutical concentration of three successive samples are the same. Positive controls are included to assess pharmaceutical sorption to the glass vial. Sorption isotherms are developed using the equilibrium sorption data; the sorption coefficient ($K_D$) is calculated for each pharmaceutical.

Experimental protocols for our degradation experiments include controls (in the absence of pharmaceutical) for (i) nitrification (i.e., ammonia + nitrite oxidation), (ii) ammonia oxidation, and (iii) nitrite oxidation. These controls characterize the microbial consortia obtained from our nitrification sequencing batch reactor before each experiment. Nitrification experiments that contain pharmaceutical are conducted in duplicate in include controls for pharmaceutical degradation during (i) ammonia oxidation when nitrite oxidation is inhibited by low concentration of sodium azide (<20 μM, (Ginestet et al., 1998)) (nitrification control), (ii) nitrite oxidation when NO2-N is added rather than NH4-N, and (iii) inhibition of ammonia oxidation using allylthiourea (ATU). Time course samples are collected to quantify pertinent solutes during the experiment. Samples are analyzed for the pharmaceutical (HPLC), pharmaceutical metabolites (HPLC), ammonia (Hach test), nitrite (IC), and nitrate (IC). Biomass for all experiments is taken from a nitrification enrichment sequencing batch reactor (Nit-SBR) maintained in the PI's laboratory. The Nit-SBR is continuously operated with a feed with ammonia and without any exogenous organic carbon. Pharmaceutical degradation data will be fit using kinetic models for each pharmaceutical that incorporate the relevant modules from the Activated Sludge Model framework (Henze et al., 2000).

**Principal Findings and Significance:**

Research in this reporting period focused on evaluating the sorption and degradation of three beta-blockers: atenolol (ATN), metoprolol (MET) and sotalol (SOT) during nitrification. Results from the batch sorption experiments suggest that sorption to biomass holds limited potential for attenuating these pharmaceuticals during wastewater treatment. Of the three beta-blockers, only MET sorbed to the inactivated nitrification SBR mixed liquor to an extent that permitted calculation of a statistically non-zero distribution coefficient ($K_D$). The measured sorption coefficient was for MET was highly dependent on experimental conditions. Two separate experiments produced $K_D$ values of 0.26 ± 0.03 and 0.09 ± 0.01 L/g-SS.

Based upon these results we undertook a more significant assessment of pharmaceutical sorption during biological wastewater treatment. The assessment examined all available (published) sorption data for pharmaceuticals - a total of 309 measured sorption coefficients that include 65 pharmaceuticals. Since the full details of the study are available in a manuscript submitted for publication in *Water Research*, focus here will be placed on the key findings. One of the aspects we wanted to explore was the role of experimental protocols (experiment type, inactivation method, etc) on the assessment of pharmaceutical sorption. It turns out that data for this type of assessment are limited by a lack of diversity in the way these experiments are conducted. Most protocols employ batch experiments with no inactivation (or the study does not report inactivation). The available data are, in many cases, characterized by a high degree of variability. This variability masks any effect related to the protocol (Figure 1 and Figure 2) (i.e., no statistically significant difference can be attributed to experimental protocols). Perhaps more importantly, the variability in the limited data suggest that suggest the experiment type (batch or continuous flow) and inactivation method (chemical, physical, or no inactivation).

Conventional wisdom suggests that the hydrophobic interactions dominate the sorption of organic chemicals to biomass. It is also common to assume equilibrium and apply a linear isotherm to describe the sorption. The combination of these assumptions has led many researchers to attempt to correlate pharmaceutical sorption (as described by a linear distribution coefficient, $K_D$) to the octanol-water distribution coefficient for the
Figure 1. Comparison of measured sorption coefficients for atenolol (ATN), carbamazepine (CBZ), diclofenac (DCF), glibenclamide (GLC), gemfibrozil (GMF), ketoprofen (KET), propranolol (PRO), sulfamethaxazole (SMX) and trimethoprim (TMP) from batch and continuous experiments. Individual data points shown using small black circles; horizontal line indicates median; mean indicated by large red circle with cross-hairs. Box extents indicate 25th (Q1) and 75th (Q3) percentile with whiskers extending to upper limit [Q3 + 1.5(Q3-Q1)] and lower limit [Q1 - 1.5(Q3-Q1)]. Also shown are p-value of one-tailed Mann Whitney test and number of data points from batch [n (batch)] and continuous [n (continuous)] experiments.
Figure 2. Measured Sorption Coefficients for atenolol (far left), carbamazepine, diazepam (middle), metoprolol and propranolol (far right) from batch and continuous experiments using chemical inactivation (e.g., NaN₃) no biomass inactivation, and physical inactivation (e.g., lyophylization). Individual data points shown using small black circles; horizontal line indicates median; mean indicated by large red circle with cross-hairs. Box extents indicate 25th (Q1) and 75th (Q3) percentile with whiskers extending to upper limit [Q3 + 1.5(Q3-Q1)] and lower limit [Q1 - 1.5(Q3-Q1)]. Also shown are number of data points (n), median log[KD(L/g-SS)] and p-value of one-tailed Mann Whitney test evaluating differences between inactivation methods (note: n/a = not applicable, i/d = insufficient data available for statistical evaluation).
Figure 3. Reported log $K_D$ values with predictions using one parameter models based on log $K_{OW}$ (top panels) and pH corrected octanol-water partitioning coefficient (log D) (bottom panels) for acidic (left), basic (middle), and multiprotic (right) PhACs using data from available sorption studies.

<table>
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<tr>
<th>Model</th>
<th>log $K_D$ (L/g-SS) =</th>
<th>n</th>
<th>adj-$R^2$</th>
<th>NSE</th>
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<tr>
<td>log $K_{OW}$ based</td>
<td>-1.700 + 0.01(log $K_{OW}$)</td>
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<td>log D based</td>
<td>-1.1895 + 0.318(log D)</td>
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<td>log $K_{OW}$ based</td>
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<td>35.4%</td>
<td>0.45</td>
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<tr>
<td>log D based</td>
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<th>$R^2$</th>
<th>NSE</th>
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<td>log $K_{OW}$ based</td>
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<td>log D based</td>
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pharmaceutical ($K_{ow}$). For pH-active molecules like most pharmaceuticals, $K_{ow}$ values must be corrected for pH. Equations (1) and (2) illustrate how $K_{ow}$ values can be corrected to produce distribution coefficients ($D$) for monoprotic acidic and basic compounds, respectively (Sangster, 1989). For multiprotic systems, where multiple species may exist in solution simultaneously, $\log D$ was calculated using Marvin 5.6.0.4, 2011, ChemAxon (http://www.chemaxon.com).

\[
\begin{align*}
D_{\text{Acidic-PhAC}} &= K_{\text{OW,Acidic-PhAC}} \left[1 + 10^{pH - pK_a} \right] \\
D_{\text{Basic-PhAC}} &= K_{\text{OW,Basic-PhAC}} \left[1 + 10^{pK_a - pH} \right]
\end{align*}
\]  

(1)  

(2)

Despite the importance of accounting of pH when assessing pharmaceutical sorption, only four studies report the pH at which the experiments were conducted (Urase and Kikuta, 2005; Abegglen et al., 2009; Horsing et al., 2011; Stevens-Garmon et al., 2011). The influence of pH can be seen in Figure 3 which shows data from these four studies. Note that attempts to correlate $K_D$ to $K_{ow}$ results in poor predictive power as assessed by adjusted $R^2$ and the Nash-Sutcliffe Efficiency (NSE) of the best fit correlations. Moreover, the pH correction fails to improve the correlations to a level that is meaningful for the prediction of pharmaceutical sorption to biomass.

These results suggest that reliance upon $K_{ow}$ and $D$ alone may be inappropriate when considering pharmaceutical sorption. Thus, we attempted to correlate the observed sorption (as described by $K_D$) to molecular descriptors of the solute including molecular weight (MW), molecular volume (MV), aromaticity, number of rotatable bonds (n.RB), hydrogen bonding capacity (hydrogen bond donors- n.HBD and acceptors- n.HBA) and polar surface area (PSA). Models of increasing complexity were systematically developed by adding one of the aforementioned predictors to the best model of with a given number of predictor variables. The performance of each model was evaluated using two main statistics – adjusted $r$-square (adj-$R^2$) and predicted $r$-square (pred-$R^2$). Model residuals were checked for homoscedasticity; multicollinearity between model variables was evaluated.

Interestingly the correlation and predictive capability for these types of models was found to plateau at approximately 60% for both acidic and basic pharmaceuticals (Figure 4). Also, the approach was ineffective for multiprotic pharmaceuticals (no models with statistically-significant parameters were found to characterize the data set). The NSEs of the best fit four parameter models are 0.622 (acidic pharmaceutical correlation) and 0.603 (basic pharmaceutical correlation), which suggests that while the best polyparameter models offer improvement over previously establish correlations, none can be characterized as having strong predictive power (i.e., NSE>0.7, McCuen et al., 2006). We hypothesize that the performance plateau results from only including solute-based descriptors, and suggest greater emphasis be placed on characterization of the sorbent in studies examining pharmaceutical sorption to suspended solids present in biological treatment units.

---

Figure 4. Evaluation of model correlation (adj-$R^2$) and predictive (pred-$R^2$) capabilities for log D based models for $K_D$ for acidic (left panel) and basic (right panel) PhACs.
To assess whether or not sorption to biomass is an important attenuation mechanism for pharmaceuticals during biological waste treatment, we examined pharmaceutical removal as a function of operational conditions (specifically SRT, MLSS and HRT) assuming a priori knowledge of $K_D$ (since our research, as described above, suggests predictive models require greater refinement). The fraction of pharmaceutical mass removal via sludge wasting ($f_{PhAC\text{-}WAS}$) was calculated as a function of $K_D$ using Equation 3.

$$f_{PhAC\text{-}WAS} = \frac{X \cdot \frac{HRT}{SRT} \cdot K_D}{1 + \left( X \cdot \frac{HRT}{SRT} \right) \cdot K_D}$$  

(3)

Where, $X$ is the biomass concentration, HRT is the hydraulic retention time and SRT is the solids retention time.

As can be seen in Figure 5, sludge wasting is most relevant for PhACs having $K_D$ greater than 1.00 L/g-SS. Note that a $K_D=1.00$ L/g-SS corresponds to the 70th percentile of all available data for pharmaceutical sorption on biomass. Consider that sludge wasting even in an activated sludge processes having a 6-hour HRT and operated at a 1-day SRT with 2 g/L MLSS (i.e., $X \cdot HRT/SRT = 0.5 \text{ gMLSS/L}$) for BOD removal (e.g., Deer Island Treatment Plant), accounts for no greater than 25% of the mass of most pharmaceuticals entering the treatment unit.

Removal of pharmaceuticals through sorption alone (via WAS) in the high-rate system is greater than 50% only if $K_D > 2.00$ L/gMLSS - a $K_D$ value which corresponds to the 77th percentile of reported values for $K_D$. Removal via WAS will be even less relevant for the majority of pharmaceuticals as the growth of activated sludge WWTPs operated at longer SRTs to achieve nutrient removal continues as WWTPs in the Northeast move towards more stringent nutrient removal targets. One option for meeting nutrient targets is through the use of MBRs. Although the high mixed liquor concentration of MBRs may be advantageous for sorption of pharmaceuticals having relatively higher $K_D$, MBRs are often used in process configurations with a long SRT (e.g., Ng and Hermanowicz, 2005). Thus, the benefit of sorption as potential pathway for pharmaceutical removal is often times offset by limited sludge wasting. For example, in an MBR operating under typical nitrifying conditions (SRT = 15 d, HRT = 8 h, MLSS = 10 g/L - i.e., $X \cdot HRT/SRT = 0.22 \text{ gMLSS/L}$), less than 10% of the mass of most pharmaceutical is removed through sorption to WAS. Results from these calculations suggest that pharmaceutical attenuation via sorption and wasting has only limited relevance in most biological treatment systems.

![Figure 5. Contour plot showing fraction of PhAC removed from a biological reactor in waste activated sludge (WAS) based on PhAC $K_D$ (x-axis) and operating conditions – MLSS($X$), HRT and SRT (y-axis).](image-url)
Research during this reporting period also examined the biodegradation of ATN, MET and SOT during nitrification. Experiments were conducted in fully aerated, 3 L borosilicate glass, batch reactors containing 400 mg/L VSS and a feedstock consisting of ammonium sulfate, potassium phosphate, and micronutrients. The initial ammonia-nitrogen concentration in each batch reactor is between 15-20 mg-N/L. Initial pharmaceutical concentration in each reactor was 20 ug/L (each pharmaceutical was evaluated separately). Concentrations of ammonia, nitrite, nitrate, biomass, and pharmaceutical were quantified over the course of a 12-hour period as described in the method section. Data were then used to model the kinetics of the nitrification process and pharmaceutical degradation in systems where ammonia oxidation was uninhibited and inhibited. Relevant data for each of these three pharmaceuticals is shown in Table 1 and the molecular structures are shown in Figure 6.

Table 1. Pharmaceuticals studied in this reporting period.

<table>
<thead>
<tr>
<th>pharmaceutical (class)</th>
<th>MW (g/mol)</th>
<th>Log $K_{OW}$</th>
<th>TPSA $(\text{Å}^2)$</th>
<th>rot. bonds</th>
<th>% aromatic carbons</th>
<th>numb. H-bond sites</th>
<th>typical trade names</th>
<th>typical concentrations in wastewater influent (ug/L)</th>
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<tbody>
<tr>
<td>Atenolol ($\beta$ blocker)</td>
<td>266.34</td>
<td>0.16</td>
<td>84.60</td>
<td>8</td>
<td>43%</td>
<td>7</td>
<td>Tenormin, Atenolol</td>
<td>2.3 (Ternes et al., 2007; Miege et al., 2008)</td>
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<tr>
<td>Metoprolol ($\beta$ blocker)</td>
<td>259.34</td>
<td>3.48</td>
<td>41.49</td>
<td>6</td>
<td>40%</td>
<td>6</td>
<td>Lopressor</td>
<td>0.21-0.25, 1.80-2.60 (Siemens et al., 2008)</td>
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<tr>
<td>Sotalol ($\beta$ blocker)</td>
<td>272.4</td>
<td>0.24</td>
<td>78.4</td>
<td>6</td>
<td>50%</td>
<td>8</td>
<td>Betapace</td>
<td>0.4 – 2.0, 0.64-0.83 (Gabet-Giraud et al., 2010) (Vieno et al., 2006)</td>
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Figure 6: Chemical structures of atenolol, metoprolol and sotalol.

To explore whether or not the presence of the pharmaceutical influences the rate of nitrification, we fit nitrification rates for the reactors on containing (~20 ug/L) pharmaceutical and those for reactors serving as the nitrification control (no pharmaceutical). For atenolol, the average nitrification rate in the control was 3.97 ± 0.42 (mg-N/g-VSSh). In each of the reactors containing the pharmaceutical, these rates were 4.00 ± 0.43, and 3.95 ± 0.53 (mg-N/g-VSSh). Therefore, it appears that atenolol has no statistically significant influence on the
nitrification process at low concentration. Similar results were found in systems containing metoprolol or sotalol—pharmaceuticals have no apparent influence on the rate of nitrification (Table 2). Note that these experiments were conducted several months apart resulting in differences in nitrification rates between experiments for the three pharmaceuticals. An important aspect of our experimental protocol is maintaining low nitrite concentration in the batch reactors. It has recently been suggested that nitrification may be responsible for some of the observed pharmaceutical biodegradation in lab studies (Gaulke et al., 2008; Gaulke et al., 2009). Nitrification rates are rarely relevant in natural or engineered environmental systems where nitrite concentrations are low. Nitrite concentrations in all batch experiments never exceeded 5 mg-N/L permitting a single step nitrification model to be employed in this phase of the research.

Table 2. Nitrification Rates (mg-Ng-VSS⁻¹h⁻¹) in Pharmaceutical Degradation Experiments

<table>
<thead>
<tr>
<th>pharmaceutical</th>
<th>control (no pharmaceutical)</th>
<th>replicate A</th>
<th>replicate B</th>
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<tr>
<td>Atenolol</td>
<td>3.97 ± 0.42</td>
<td>4.00 ± 0.43</td>
<td>3.95 ± 0.53</td>
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<tr>
<td>Metoprolol</td>
<td>5.62 ± 0.44</td>
<td>5.70 ± 0.47</td>
<td>5.49 ± 0.42</td>
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<tr>
<td>Sotalol</td>
<td>2.88 ± 0.39</td>
<td>2.83 ± 0.39</td>
<td>2.95 ± 0.40</td>
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The batch experiments were also designed to assess the potential of the nitrifiers to degrade the selected pharmaceuticals. Results indicate that atenolol was degraded during nitrification whereas no degradation was observed for metoprolol or sotalol. Interestingly, atenolol biodegradation was also noted in the nitrification inhibition control reactor (275 µM ATU for nitrification inhibition). Atenolol degradation was modeled using pseudo first order kinetics. The VSS normalized, pseudo first-order rate coefficients for the two replicate reactors containing atenolol were 2.33 ± 0.45 Lg-VSS⁻¹d⁻¹ and 2.65 ± 0.92 Lg-VSS⁻¹d⁻¹. The rate coefficient for the reactor in which nitrification was inhibited was 0.577 ± 0.45 Lg-VSS⁻¹d⁻¹. The degradation rate of atenolol in the presence of nitrification in these experiments in more than four times faster than the rate when nitrification is inhibited. We suspect that the degradation in the inhibited system is the result of some heterotrophic degradation. Work in the coming period will assess this through a series of additional experiments, some of which will be focused on elucidating biomass populations. Specifically, the degradation of atenolol during nitrite oxidation will be assessed to evaluate the observed degradation of atenolol in the nitrification inhibition experiment is a result of the activity of nitrite oxidizing bacteria. In addition, we anticipate completing DNA extraction for the samples from experiments conducting and analyzing the DNA using quantitative real-time PCR (qPCR) to elucidate the relative concentrations of ammonia oxidizing, nitrite oxidizing, and heterotrophic bacteria. Data from experiments evaluating degradation of atenolol and naproxen during nitrification (note that experiments with naproxen were completed prior to the reporting period) will be modeled within the framework of the Activated Sludge Model framework (Henze et al., 2000).

Work in the coming period will also focus on evaluating the degradation of diazepam, and possibly some structurally similar pharmaceuticals, during nitrification. Diazepam is a Schedule IV controlled substance which requires State and Federal registration before research can commence. State registration was obtained on 27 Feb 2012, and we are in the final stages of the Federal registration process.

Student Support

1. Sandeep Sathyamoorthy, PhD Candidate, Environmental and Water Resources Engineering program, Department of Civil and Environmental Engineering, Tufts University

2. Catherine Hoar, BS Environmental Engineering student, Department of Civil and Environmental Engineering, Tufts University
Notable Achievements and Awards
Nothing to report at this time.

References


Stephenson, R. and J. Oppenheimer (2007). Fate of Pharmaceuticals and Personal Care Products Through Municipal Wastewater Treatment Processes, WERF.


Assessing Human Impacts on Sediment and Contaminant Trapping within Oxbow Lake, Northampton, Massachusetts

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Publications

Problem and Research Objectives: To assess deposition rates and associated contaminant inventories within Connecticut River floodplain lakes and ponds and how they have changed through time in response to both natural processes and man-made disturbances.

Methodology: Evaluates changes in sediment and heavy metal accumulation from Oxbow Lake in Northampton, MA as a case study using a combination of sediment cores and geophysical surveys.

Principal Findings and Significance: The magnitude of deposition in Oxbow Lake over the last hundred years was observed to be roughly equivalent to maximum water depths in the lake and point to the rapid infilling in recent centuries. The timing for the onset of rapid infilling occurs contemporaneous with the documented creation and beginning of routine maintenance of the tie-channel connecting the lake to the main river, followed shortly after by a rapid rise in heavy metal concentrations related to industrial activity along the river. Mercury concentrations are particularly high in recent sediments, with peak concentrations reaching ~500 ppb. Results point to the creation and routine maintenance of inlets increasing the connectivity of off-river waterbodies to the main river in recent centuries, and the enhanced sediment trapping along the floodplain at an optimal time for capturing legacy contaminants introduced during the industrial era.

The effects of Hurricane Irene on the Connecticut River during the project provide rare insight into the depositional response of backwater floodplain environments like Oxbow Lake to an extreme precipitation event. Torrential rains from the Irene event resulted in flash-flooding within the uplands of the Connecticut River. Here excessive channel erosion and landscape disturbance provided widespread access to glaciolacustrine sediments common to the uplands of many Atlantic draining rivers. Once mobilized, these fine grained sediments were rapidly transported to downstream, diluting particulate organics, and capping contaminated industrial depocenters like Oxbow Lake with a relatively clean, inorganic, clay/silt layer.

Student Support

Two students pursuing Master of Science degrees in Geosciences were supported with funds and matching funds associated with this grant.
Authentic Research Projects for Undergraduates based on Groundwater Contamination Issues Related to Arsenic

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Publications

There are no publications.
**Problem and Research Objectives:** The goal was to devise authentic research projects for undergraduates based on groundwater contamination issues related to arsenic. In particular, the possibility of examining both (a) the mechanisms by which arsenic is dissolved in the shallow aquifers in counties like Bangladesh, and (b) some strategies for remediation of contaminated water by low-cost, readily available materials.

**Methodology:** Some preliminary experiments were conducted by a graduate student over the summer under the direction of Professor Tyson, who also worked on the project, and who enlisted the help of some high school teachers, present for a week’s workshop. Professor Tyson then created projects for groups of undergraduate students from the honors first-year class to work on in both the fall and the spring semester. Each project team was led by a graduate student (including the student funded by the grant) or by an experienced upper-level undergraduate.

**Principal Findings and Significance:**
In the fall, the relevant group themes consisted of (1) dissolution of arsenic sulfide minerals, (2) removal of arsenic from contaminated water by moldy biomass, and (3) removal of arsenic from contaminated water by coffee grounds (a form of biochar). In the spring, relevant themes were (1) removal of arsenic from contaminated water by wood biochar, and (2) coffee grounds. Over the two semesters there were 10 projects in total. It proved difficult to obtain arsenic sulfide minerals. Initial, promising results with the coffee grounds was mitigated by the discovery that an extracted chemical (or chemicals) interfered with the measurement. Biochar containing iron is very promising. All of the projects were sufficiently challenging to engage the students fully during the semester, and the self-reported satisfaction was very high. The biologically mediated remediation was less convincing, and although the students were challenged, this may not be a promising line of investigation. Part of the problem is that food spoilage molds are quite difficult to culture on food that contains preservatives.

**Student Support**
One graduate student was supported. She is pursuing a doctoral degree in analytical chemistry.

**Notable Achievements and Awards**
This was a relatively modest project, but has opened up a new area of investigation for the undergraduate arsenic groups, namely the potential of remediation of contaminated water by biochar materials. During the period of the award, Professor Tyson was awarded a small grant by the Analytical Division of the American Chemical Society to create a public lecture/demonstration concerning the impact of arsenic compounds in the environment, which was delivered in December 2011. He has also been invited to contribute a book, in the John Wiley Analytical Chemistry Series, on much the same topic. The book will include a chapter on engaging undergraduate students in authentic research experiences.
USGS Award # G11AP20227 Development of a Hydroclimate Synthesis Report for International Upper Great Lakes Study

Basic Information

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<td>Casey Brown</td>
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Publication

Annual Report (from March 1, 2011 to February 28, 2012)

Title: Development of a Hydroclimate Synthesis Report for International Upper Great Lakes Study

Project Number: USGS Award # G11AP20227

Problem and Research Objectives:
The fundamental goal of this Synthesis was to prepare a comprehensive report on the conceptual underpinnings of the strategy that the IUGLS took with respect to climate change impact analysis, and its relationship to the development of Lake Superior regulation plan options.

Methodology:
Current findings of the IUGLS as well as relevant findings in the peer reviewed literature were reviewed and synthesized to produce a single document to guide decision making in the selection of a new regulation plan for the Upper Great Lakes.

Principal Findings and Significance:
The report led to the adoption of an adaptive management strategy in order to address uncertainty on the Upper Great Lakes.

Student Support
The funding provided partial support for 1 MS and 1 PhD student.

Notable Achievements and Awards

Publications and Conference Presentations:
Provide citations for publications resulting from all projects supported using your grant and required matching funds, including base grants. Please provide the citations in the format requested.

a. Articles in Refereed Scientific Journals

b. Book Chapter

c. Dissertations

d. Water Resources Research Institute Reports

e. Conference Proceedings

f. Other Publications
# USGS Award No. G11AP20228 Climate Risk Assessment and Management

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## Publications

There are no publications.
Problem and Research Objectives:
The overarching objective of this effort is to develop methods for vulnerability assessment and risk evaluation that can be applied to assist in water management risk-informed decision making. The U.S. Army Corps of Engineers (USACE) is contributing toward the development of a risk management framework for incorporating the uncertainty of future climate change into decision making. The framework is intended to be applied across a project’s entire lifecycle, since climate change uncertainty may require making sequential decisions over time and updating design and plans as more is learned. One of the critical next steps is to develop approaches that can be applied to water management. Water management decisions require trading off conflicting objectives that affect many groups of stakeholders. The work effort is developing procedures to assess the vulnerabilities of a water resources project or system of projects to climate change and variability. The information can then be used for risk evaluation of the water management system under future climate conditions. The methods developed in this study should support the development of guidance for incorporating climate change considerations into water management. The methods should be useful for revising water management operating plans and reservoir reallocation studies.

Methodology:
1. Vulnerability Assessment. The goal of this step is to develop "bottom-up" vulnerability assessment methods for multi-objective water management. The vulnerability assessment will identify what type of climate changes or variability causes problems for the system. The process can identify the potential thresholds where system performance begins to degrade and other conditions that cause severe problems for the system. 2. Risk Assessment and Evaluation. Risk is defined by the consequences and likelihood of an event. The results of the vulnerability assessment can be used to determine consequences from potential climate events. The likelihood of an event may be based on a wide range of climate information including historical information, climate model projections, stochastic simulations, and paleo-climatological information. 3. Risk Informed Decision Making and Adaptive Management Strategies. The overall aim of the risk evaluation is to better inform water management decisions. This step will support the development of risk management strategies for water management. Given the uncertainties associated with future climate, adaptive management strategies may perform better for a wider range of future climate conditions and be more responsive to changing conditions.

The process is being applied to a case study of the Coralville Reservoir in Iowa.

Principal Findings and Significance:
The work is ongoing but the framework shows promise and USACE is considering for broad application to federal water projects.

Student Support
The funding provides partial support for 1 MS student.
Notable Achievements and Awards

Publications and Conference Presentations:
Provide citations for publications resulting from all projects supported using your grant and required matching funds, including base grants. Please provide the citations in the format requested.

a. Articles in Refereed Scientific Journals

b. Book Chapter

c. Dissertations

d. Water Resources Research Institute Reports

e. Conference Proceedings

f. Other Publications
Information Transfer Program Introduction

A significant portion of 104B funds retained at the Center supports the information transfer objective of 104B.

Our main information transfer tool is the Annual Water Resources Conference, initiated in 2003 by then Director David Reckhow. The conference provides an interdisciplinary forum for scientists, practitioners, and policy makers to discuss current critical water research, foster greater collaboration among scientists and practitioners, and strengthen the connection between research, education, and policy. Participants include researchers, stakeholders, and managers of water resources from academia, government, non-profits, and the private sector. The 8th Annual Water Resources Research Center Conference is described in the subsequent section. The Center publishes programs from all of our conferences on our website <http://www.umass.edu/tei/wrrc/WRRC2004/WRRCconferences.html> (will move to www.wrrc.umass.edu in July 2012).
Water Resources Research Conference

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Publication

The Water Resources Research Center organized the eighth annual Water Resources Conference on the UMass Amherst campus on April 7, 2011. While the conference took place in April 2011, most of the work for this conference was accomplished in the reporting period. The Cooperative State Research, Education, and Extension Service New England Regional Program again cooperated in planning the conference. Four additional co-sponsors helped underwrite the cost of the conference.

Thirty-two posters were presented and there were 30 platform presentations in three concurrent sessions. The presentations were grouped into the following 9 sessions:

- Climate Change and Stream Crossings in the Northeast
- Monitoring and Detecting Harmful Algal Blooms
- Nutrients Management in Water
- Climate Change Adaptation Implementation Strategies
- Fish Passage and Stream Continuity
- Findings of the Connecticut River Targeted Watershed Initiative
- Climate Change Adaptation and Decision Making
- Tools for Water Management in the Connecticut River Basin
- Stormwater and Low Impact Development

There were three Plenary Addresses at the beginning of the conference:

- “The University Perspective” by Rick Palmer, Professor and Department Head, Dept. of Civil and Environmental Engineering, UMass Amherst
- “The State of Massachusetts Perspective” by Vandana Rao, Assistant Director for Water Policy, Mass. Executive Office of Energy and Environmental Affairs

The Keynote Address was given by Dr. Richard Vogel, Professor of Civil and Environmental Engineering and Director of the Graduate Program in Water: Systems, Science and Society, Tufts University, on “Water Resources Planning in a Changing World.”

181 people registered for the event, representing 14 colleges and universities, 23 companies, 15 governmental agencies, 4 non-profit organizations, and 13 municipalities.

Twenty-four students (from 6 different institutions) participated in the Best Student Poster Competition, evaluated by 14 judges. Liam Bevan of UMass Amherst Geosciences (and a WRIP research project awardee this fiscal year) and Barbara DeFlorio of UMass Amherst Veterinary & Animal Sciences tied for first place. Bevan’s poster was entitled “Water Flux at Till/ Bedrock Interfaces in Central Massachusetts.” DeFlorio’s poster’s title was: “Optimizing Vegetative Filter Strips Treating Runoff from Turf.”

**Students supported by project**
1 BS student in Mathematics at UMass Amherst
1 BS student in Chemical Engineering at UMass
None.
Notable Awards and Achievements